

Uptake of Excess CO₂ by an Outcrop-Diffusion Model of the Ocean

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A carbon cycle model is presented in which direct ventilation of intermediate and deep ocean waters in high latitudes is taken into account. The 1½-dimensional ocean model is an extension of a box-diffusion model including a deep-sea outcrop at the surface. If both are calibrated in a consistent way, the outcrop-diffusion ocean takes up more excess CO₂ than the box-diffusion ocean because the outcropping deep water is essentially virgin as to fossil CO₂. Two calibration methods are compared, using the distribution either of natural or of bomb-produced ¹⁴C. The latter leads to a higher oceanic uptake of excess CO₂ than the former and to a better agreement with the observed atmospheric increase. Long-term model responses are also discussed.

INTRODUCTION

Between 1959 and 1978, the mean atmospheric CO₂ level as measured at Mauna Loa, Hawaii, and at the South Pole increased from 315.6 to 333.8 ppm [Bacastow and Keeling, 1981], which corresponds to 55% of all fossil CO₂ produced in that period (69.8×10^{15} g C, equivalent to 32.9 ppm; Rotty [1982]), with an estimated uncertainty of 5 to 10%. There are strong indications that the biosphere, through the destruction of biomass, has been an additional net CO₂ source that cannot be assessed quantitatively, however. If this is the case, the actual airborne fraction, referring to the total CO₂ input, is smaller than the above value. Existing models of the global carbon cycle in general predict that the ocean has taken up less than the nonairborne fraction of 45% of all fossil CO₂ (problem of the 'missing sink'). The question is, therefore, do important processes not included in these models exist and is the oceanic uptake actually larger than their results indicate.

The transport of excess CO₂ from the atmosphere into the interior of the ocean is limited by two kinds of transport resistances: gas exchange between air and water, controlled by diffusion through a thin water film at the surface, and oceanic mixing, responsible for the exchange between the surface and deeper layers. According to one-dimensional models, the resistance connected to air-sea exchange is of minor importance. However, a process not accounted for by simple one-dimensional models is the direct ventilation of the deep sea in its outcropping regions in high latitudes [Broecker et al., 1980; Oeschger et al., 1980]. In these regions of deepwater formation, vertical mixing is much faster than near the surface of the warm water sphere because of deep convection. This is, for instance, reflected in the fact that bomb-produced ¹⁴C and tritium have penetrated to great depths in the deepwater outcropping regions and have relatively low surface concentrations there because of the large diluting volume [Östlund and Fine, 1979; Stuiver and Östlund, 1980; Östlund and Stuiver, 1980]. In these regions the rate of gas exchange becomes important for the overall transport.

Craig [1963] introduced the concept of a deepwater outcrop for a model of the global cycle of ¹⁴C without considering CO₂ perturbations. Broecker et al. [1971] discussed the

possible influence of the direct exchange between atmosphere and deep sea, using a diffusive ocean model in an approximate way. Later, other authors included deepwater formation in their models by introducing an advective flux from a surface mixed layer to the deep sea [Björkström, 1979; Hoffert et al., 1981], but in this way they left out the feature that is actually important for the atmospheric CO₂, namely the contact of deep water (which is nearly virgin with respect to excess CO₂) with the atmosphere. Recently, rapid vertical exchange in high-latitude regions has been considered in several papers [Takahashi and Azevedo, 1982; Crane, 1982; Kratz et al., 1983].

It is the aim of this paper to study the significance of the direct atmosphere-deep sea exchange for the oceanic uptake of CO₂ and ¹⁴C by means of a simple model which is an extension of the box-diffusion (BD) model of Oeschger et al. [1975]. Furthermore, the influence of the method of calibration of the model is considered. The dynamic model parameters concerning the ocean have often been determined from the distribution of natural ¹⁴C in the oceans. Thanks to the GEOSECS program, a set of ¹⁴C data has become available that permit a model calibration based on bomb-produced ¹⁴C. Broecker et al. [1980] showed that this second method of calibration yields higher transport rates. The two methods are compared below.

MODEL EQUATIONS OF THE OUTCROP-DIFFUSION (OD) MODEL

For correctly simulating atmospheric concentration changes and air-sea fluxes of CO₂ and ¹⁴C, a model should also correctly reproduce the mean concentration changes at the ocean surface, but it need not necessarily be a realistic picture of processes in the interior of the ocean. The present model is designed with emphasis on atmospheric perturbations; consequently, some internal ocean processes, such as particulate transport of carbon and nutrients, are neglected. It is, however, clear that for studying the stationary distribution of carbon or the cycling of oxygen and nutrients, these processes cannot be neglected [cf. Bolin et al., 1983].

Figure 1 shows the idea on which the model is based. The major (warm) part of the surface is covered by a mixed layer of 75-m depth; the deep sea below it is vertically mixed by eddy diffusion and reaches the (cold) surface in high latitudes. The reservoir 'deep sea' also includes the thermocline waters. Along the surfaces of equal density (isopycnals; dashed lines in Figure 1) that connect the deep waters with the outcrop region, mixing is infinitely rapid. This assumption

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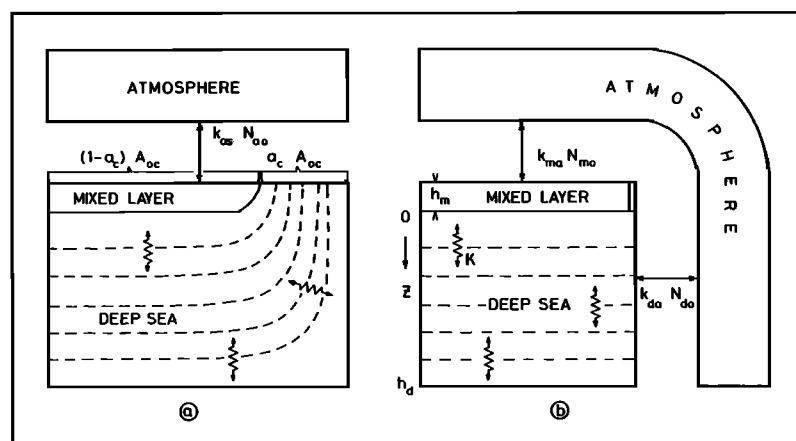


Fig. 1. Scheme of the outcrop-diffusion model: (a) physical idea; (b) mathematical representation.

tion is, of course, an oversimplification, and the model has therefore to be considered as an extreme case with respect to isopycnal mixing. However, its mathematics can be treated relatively easily, while a finite rate of horizontal mixing would imply considerable complications. The isopycnals are inclined only very little in reality so that they can be regarded as horizontal. The vertical eddy diffusion of the model can be regarded as a parameterized representation of all the various processes of mixing and advection in the ocean, projected on a vertical axis. In particular, it also represents mixing along inclined isopycnal surfaces. If K_h is the quasihorizontal diffusivity and $\alpha = L_v/L_h$, where L_v and L_h are characteristic vertical and horizontal lengths, then the vertical component of diffusion has the diffusivity

$$K_v = \alpha^2 K_h = (L_v/L_h)^2 K_h \quad (1)$$

With $K_h \sim 10^7 \text{ cm}^2 \text{ s}^{-1}$ [Okubo, 1971] and $L_v \sim 1 \text{ km}$ and $L_h \geq 10^3 \text{ km}$, we can expect a corresponding K_v of the order of 1 to $10 \text{ cm}^2 \text{ s}^{-1}$, which is actually found (see below).

About 10 to 20% of the total carbon transport from the

surface to the deep sea is accomplished by solid biogenic particles. This is neglected in the model because the emphasis here is on CO₂ perturbations. Biological productivity is limited by availability of phosphorus and nitrogen and does not increase with higher CO₂ levels. In the mathematical model the outcrop region (vertical in Figure 1b) covers the fraction a_c of the total ocean surface. The atmosphere is in exchange with all layers of the deep sea, and the stationary CO₂ exchange flux per unit depth through the outcrop is independent of depth, i.e., bottom waters and intermediate waters are ventilated at an equal rate. The ocean is horizontally homogeneous.

The model equations are derived similarly as the BD model of Oeschger *et al.* [1975], so that not all details are reported here. For a general discussion of modeling concepts, see Bolin [1981]. The preindustrial, steady state CO₂ exchange fluxes between atmosphere and mixed layer or deep-sea outcrop are called F_{am} and F_{ad} , respectively (units: moles C per m² of ocean surface per year). If the atmospheric concentration is increased by the fraction ν_a , the fluxes

TABLE 1. Main Quantities and Parameters Used in the Calculations

Symbol	Meaning	Value
N_{ao}	CO ₂ in pre-industrial atmosphere (290 ppm)	$615.6 \times 10^{15} \text{ g C}$
$N_{oc,t}$	Carbon in preindustrial ocean	$38,400 \times 10^{15} \text{ g C}$
N_{bo}	Carbon in preindustrial biosphere	$2.4 N_{ao}$
C_o	Preindustrial concentration of total CO ₂ in surface water	2.052 mol m^{-3}
A_{oc}	Ocean surface area	$3.62 \times 10^{14} \text{ m}^2$
h_a	Thickness of ocean layer containing as much carbon as preindustrial atmosphere	about 69 m
h_{oc}	Average depth of ocean	3729 m
h_m	Depth of mixed layer (warm surface ocean)	75 m
a_c	Relative area of outcrop (cold surface water)	variable
F_{as}	Preindustrial average CO ₂ exchange flux atmosphere—surface ocean	(see text)
k_{ij}	Exchange coefficient between reservoirs i and j	$k_{ij} = F_{ij}/N_{i0}$
k_{ba}	Exchange coefficient biosphere—atmosphere	1/60 yr
K	Eddy diffusivity	(see text)
ξ_m	Buffer factor for warm surface (mixed layer) water	9*
ξ_t	Buffer factor for cold surface water	14*
λ	¹⁴ C decay constant	1/8267 yr
R_{ao}	¹⁴ C concentration of preindustrial atmosphere	1
R_{mo}	¹⁴ C concentration of preindustrial mixed layer	0.95†
R_{do}	Average ¹⁴ C concentration of preindustrial deep sea below 75 m	0.84†

*Values adopted for analytical calculations; for numerical simulations slightly different values were assumed, see text.

†Values adopted for calibration 1; for calibration 2, see text.

into the ocean increase in proportion, and the (gross) flux from atmosphere to mixed layer is then $F_{am}(1 + \nu_a)$. The back flux from sea to air increases more strongly than the concentration of total dissolved CO₂ in surface water (relative increases ν_m in mixed layer and $\bar{\nu}_d$ on the average in deep sea) because the relative change of the partial pressure of CO₂ is stronger by a factor ξ (buffer factor) than the relative change of total dissolved CO₂, as the result of a shift of the chemical equilibria between the different chemical species: CO₂, HCO₃⁻ and CO₃⁼. It is convenient to write the preindustrial atmospheric CO₂ amount as $N_{ao} = C_o h_a A_{oc}$, where C_o is the total CO₂ concentration in surface water and A_{oc} the surface area of the ocean. From the GEOSECS data, $C_o = 2002 \mu\text{mol/kg}$ [Takahashi *et al.*, 1981b]; $A_{oc} = 3.62 \times 10^{14} \text{ m}^2$ [Menard and Smith, 1966]. With a preindustrial atmospheric level of 290 ppm, $N_{ao} = 615.6 \times 10^{15} \text{ g C}$, which yields an equivalent height of the atmosphere $h_a = 69.0 \text{ m}$ [Bacastow and Björkström, 1981]. Noting that the mixed layer area is $(1 - a_c)A_{oc}$ and the outcrop area is $a_c A_{oc}$, the CO₂ balance for the atmosphere is (the main symbols are summarized in Table 1):

$$A_{oc} h_a C_o \frac{d\nu_a}{dt} = q + (1 - a_c) A_{oc} F_{am} (\xi_m \nu_m - \nu_a) + a_c A_{oc} F_{ad} (\xi_d \bar{\nu}_d - \nu_a) \quad (2)$$

where q is the anthropogenic CO₂ production rate.

With the exchange coefficients

$$k_{am} = \frac{(1 - a_c) F_{am}}{h_a C_o} \quad k_{ad} = \frac{a_c F_{ad}}{h_a C_o} \quad (3)$$

(1) becomes

$$\frac{d\nu_a}{dt} = \frac{q}{N_{ao}} + k_{am} (\xi_m \nu_m - \nu_a) + k_{ad} (\xi_d \bar{\nu}_d - \nu_a) \quad (4)$$

The vertical diffusive flux per unit area in the deep sea is $-K \partial C / \partial z = -K C_o \partial \nu_d / \partial z$ (C = total CO₂ concentration). Then the CO₂ balance for an infinitesimal layer between depths z and $z + dz$ reads

$$A_{oc} \frac{\partial C}{\partial t} = A_{oc} K \frac{\partial^2 C}{\partial z^2} + \frac{a_c A_{oc} F_{ad}}{h_d} (\nu_a - \xi_d \nu_d) \quad (5)$$

Note for the last term that the exchange through the outcrop is $a_c A_{oc} F_{ad}$ for the whole deep sea but only the fraction dz/h_d of that for a layer of thickness dz . Thus the water is ventilated everywhere at the same rate, independent of depth. Division by $A_{oc} C_o$ yields

$$\frac{\partial \nu_d}{\partial t} = K \frac{\partial^2 \nu_d}{\partial z^2} + k_{da} (\nu_a - \xi_d \nu_d) \quad (6)$$

where

$$k_{da} = a_c F_{ad} / C_o$$

The CO₂ balance for the mixed layer is (leaving away the area A_{oc})

$$(1 - a_c) h_m C_o \frac{d\nu_m}{dt} = (1 - a_c) F_{am} (\nu_a - \xi_m \nu_m) + K \frac{\partial C}{\partial z} \quad z = 0 \quad (7)$$

or

$$\frac{d\nu_m}{dt} = k_{ma} (\nu_a - \xi_m \nu_m) + \frac{1}{(1 - a_c) h_m} K \frac{\partial \nu_d}{\partial z} \quad z = 0 \quad (8)$$

where

$$k_{ma} = \frac{F_{am}}{h_m C_o}$$

While the mixed layer covers only the area $(1 - a_c)A_{oc}$, diffusive downward transport into the deep sea is formulated here as occurring through the whole deep sea area A_{oc} . In addition to (4), (6), and (8), the boundary conditions at the bottom (no flux) and at the boundary mixed layer-deep sea (continuity of concentration) are needed:

$$\begin{aligned} \frac{\partial \nu_d}{\partial z} &= 0 & z &= h_d \\ \nu_m &= \nu_d & z &= 0 \end{aligned} \quad (9)$$

For ¹⁴C the buffer factors can be omitted, and terms for the radioactive decay have to be added. In this study, which concentrates on ocean modeling, the biosphere is assumed to be neutral with respect to CO₂. For ¹⁴C perturbations, however, it has to be included because biospheric carbon provides for a relatively large diluting reservoir, e.g., by taking up bomb ¹⁴C. It is simulated by an exponential box as by Siegenthaler and Oeschger [1978]. If $R_i(t)$ is the ¹⁴C concentration in reservoir i (corrected to $\delta^{13}\text{C} = -25\text{‰}$ O), the balance equations are

$$\begin{aligned} \frac{d}{dt} R_a (1 + \nu_a) &= \frac{^{14}q}{N_{ao}} + k_{am} (R_m [1 + \xi_m \nu_m] - R_a [1 + \nu_a]) + k_{ab} (R_b - R_a) + k_{ad} \\ &\cdot (\bar{R}_d [1 + \xi_d \bar{\nu}_d] - R_a [1 + \nu_a]) - \lambda R_a (1 + \nu_a) \end{aligned} \quad (10)$$

$$\frac{dR_b}{dt} = k_{ba} (R_a - R_b) - \lambda R_b \quad (11)$$

$$\begin{aligned} \frac{\partial}{\partial t} R_d (1 + \nu_d) &= K \frac{\partial^2}{\partial z^2} R_d (1 + \nu_d) + k_{da} (R_a [1 + \nu_a] - R_d [1 + \xi_d \nu_d]) - \lambda R_d (1 + \nu_d) \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{d}{dt} R_m (1 + \nu_m) &= k_{ma} (R_a [1 + \nu_a] - R_m [1 + \xi_m \nu_m]) \\ &+ \frac{1}{(1 - a_c) h_m} K \frac{\partial}{\partial z} R_d (1 + \nu_d) \Big|_{z=0} - \lambda R_m (1 + \nu_m) \end{aligned} \quad (13)$$

From the atmosphere-biosphere exchange flux F_{ab} , which is taken as constant in time, the corresponding exchange coefficients are defined by

$$\begin{aligned} k_{ab} &= \frac{N_{ao}}{F_{ab}} \\ k_{ab} &= \frac{N_b}{F_{ab}} \end{aligned} \quad (14)$$

LINEARIZED PERTURBATION EQUATIONS FOR ¹⁴C AND NUMERICAL MODEL

Equations (10) to (13) can in principle be used for numerical simulations in the form given above. However, it is

preferable to rewrite them as perturbation equations, because for relatively small perturbations, such as the Suess effect, rounding errors arising in the numerical procedures may become significant if the computations are done with the absolute concentrations R_i . The relations for CO₂, (4), (6), (8), and (9) are already in a perturbation form.

The exact perturbation equations are somewhat complicated, and linearized relations are used here. For the atmosphere this yields ($r_i = R_i - R_{io}$, deviation from steady state ¹⁴C concentrations; $^{14}q = ^{14}C$ production rate)

$$\frac{dr_a}{dt} = \frac{^{14}q}{N_{ao}} - \frac{q}{N_{ao}} - \lambda r_a + k_{am}(r_m - r_a) + k_{ad}(\bar{r}_d - r_a) + k_{ab}(r_b - r_a) \quad (15)$$

This is analogous to (4) for CO₂, except for the source/sink terms, the buffer factors ξ_i that are to be set 1, and the additional biospheric exchange term. The equations for the other reservoirs are analogous to those for CO₂, with similar changes as for the atmosphere.

The errors committed by using these approximate equations are estimated to affect the results for the perturbations to a few percent at maximum. Numerical computations were performed by means of the simulation language CSMP III. The deep sea reservoir was split up into 42 levels, 25 m apart between 75-m and 1000-m depth and 545.8 m apart between 1000-m depth and the seafloor. The spatial derivatives were approximated by using a second-order difference scheme [Heimann, 1978]. Numerical computations were carried out only for $a_c = 0$ and $a_c = 0.1$.

MODEL CALIBRATION BY MEANS OF PREINDUSTRIAL ¹⁴C

As far as possible, values of the relevant model quantities and parameters (Table 1) were taken from independent sources. Reservoir sizes generally correspond to those given by Bacastow and Björkström [1981]. The effective atmospheric depth h_a (69 m for 290 ppm) is considerably larger than in the original BD papers [Oeschger et al., 1975; Siegenthaler and Oeschger, 1978; Oeschger et al., 1980]. In those papers, h_a (58 m) was calculated on the basis of a mean value of dissolved inorganic carbon for the whole ocean instead of for the surface ocean only. This influences the results for the airborne fraction for which, now, higher values are obtained than for $h_a = 58$ m.

Different criteria may be thought of for determining the outcrop area. For instance, it might be identified with the cold sea surface (temperatures below 5°C), which covers about 10% of the open surface of the world ocean. The regions where deep convection leads to the formation of deep water cover much less than 10% of the ocean surface, but the model outcrop partly represents, beside the regions of deepwater formation, the outcrop of thermocline waters. Thus values between 0.05 and 0.15 for a_c seem acceptable.

Buffer factors for different regions of the world ocean were calculated by Takahashi et al. [1980]. From their data I choose $\xi_m = 9$ and $\xi_d = 14$ for the analytical solution as well as for the pulse response (see below), and

$$\xi_i = \xi_{io} + 4.9 \xi_i \nu_i - 0.1(\xi_i \nu_i)^2 \quad (16)$$

($i = m, d$; $\xi_{mo} = 9$, $\xi_{do} = 14$) for the numerical version of the model. Equation (16) takes into account that the oceanic CO₂ uptake capacity decreases with increasing pCO_2 ; $\xi_i \nu_i$ is

the relative increase of pCO_2 ; the coefficients of $\xi_m(\nu_m)$ were determined from Figure 3 of Bacastow and Keeling [1973] and adopted also for $\xi_d(\nu_d)$.

For the CO₂ production rate, the data compiled by Keeling [1973b] were used from 1860 to 1950 and those of Rotty [1982] from 1950 to 1980. For the analytical solution a preindustrial CO₂ level of 290 ppm is adopted. For the numerical simulations the preindustrial (1860) value is adjusted such that the simulation yields the observed value of 315.6 ppm at the beginning of 1959 (average of Mauna Loa and South Pole) [Bacastow and Keeling, 1981]. The preindustrial levels obtained are 292.8 for BD and 295.8 ppm for OD, with $a_c = 0.1$ (cf. Table 3).

The two principal dynamic parameters, the eddy diffusivity K and the air-sea exchange flux F_{as} , were determined in two ways. The first calibration method, also used in previous studies [e.g., Broecker et al., 1971; Keeling, 1973a; Oeschger et al., 1975; Bolin, 1981] is to prescribe the preindustrial ¹⁴C distribution in the ocean. The idea behind this is that, ideally, a model should be able to consistently simulate different phenomena of the global carbon cycle, in particular the steady state ¹⁴C distribution, the anthropogenic CO₂ increase, and the corresponding ¹⁴C dilution (Suess effect), as well as the partitioning of bomb-produced ¹⁴C between atmosphere, biosphere, and ocean. The present model, however, is not so ideal, so another calibration method by means of bomb-produced ¹⁴C will also be discussed below.

The preindustrial values assumed are $R_{ao} = 100\%$ for the atmosphere, $R_{mo} = 95\%$ for the warm mixed layer, and $\bar{R}_{do} = 84\%$ for the deep sea below 75 m. The mean ¹⁴C concentration for the whole ocean is then found to be $R_{oc,o} = 84.2\%$.

The global exchange flux $A_{oc} F_{as}$ between atmosphere and surface ocean is determined from a steady state balance between ¹⁴C influx into the ocean and radioactive decay:

$$A_{oc} F_{as} (R_{ao} - \bar{R}_{so}) = \lambda N_{oc,t} \bar{R}_{oc,o} \quad (17)$$

Here $N_{oc,t}$ denotes the actual total amount of dissolved carbon in the ocean (including organic carbon). In contrast, C_o , as used in the perturbation equations, is the mean concentration of dissolved inorganic carbon in surface water and is about 13% lower than the mean value for the whole ocean. With this calibration the (gross) perturbation fluxes are correctly given by $\nu_a F_{as}$, $\xi_m \nu_m F_{am}$, and $\nu_d \nu_d F_{ad}$.

On the other hand, the model-predicted stationary ¹⁴C values with constant CO₂ concentration C_o for the ocean, if computed with the exchange flux according to (17), would be higher than the prescribed values R_{mo} and R_{do} . This inconsistency arises because the carbon transport by organic and carbonate particles, which is not important for CO₂ perturbations, is neglected. The stationary profile must therefore be computed by using a smaller flux:

$$F_{as}^* = F_{as} C_o A_{oc} h_{oc}/N_{oc} \quad (18)$$

Analogously, the fluxes F_{am}^* and F_{ad}^* (and the exchange coefficients k_{ma}^* and k_{da}^* , see below) are related to the nonstarred quantities by the factor $C_o A_{oc} h_{oc}/N_{oc}$.

The ¹⁴C concentration in the mixed layer is fixed, but \bar{R}_{so} , and therefore F_{as} , depends on the outcrop area a_c ; the resulting values for F_{as} are given in Table 2. The preindustrial values obtained are 18.0 and 13.3 mol m⁻²yr⁻¹ for $a_c = 0$ and 0.1, respectively; the corresponding atmospheric CO₂

TABLE 2. Analytical Model Results as a Function of Outcrop Area a_c

a_c	r_a	r_m	r_d	e_m	e_d	K	F_{as}
<i>Calibration with Preindustrial ¹⁴C</i>							
0.0	0.667	0.333	0.000	0.826	0.105	4005	17.99
0.02	0.647	0.302	0.051	0.819	0.118	3529	16.76
0.05	0.626	0.266	0.108	0.809	0.133	2948	15.24
0.10	0.605	0.221	0.173	0.795	0.149	2224	13.32
0.20	0.585	0.164	0.251	0.769	0.167	1312	10.86
<i>Calibration with Bomb ¹⁴C</i>							
0.0	0.611	0.389	0.000	0.806	0.143	7685	20.63
0.10	0.528	0.271	0.202	0.801	0.213	5180	19.26

Airborne fraction (r_a), oceanic uptake of excess CO₂ entering via mixed layer (r_m) and deep-sea outcrop (r_d), degrees of equilibrium of mixed layer (e_m) and outcrop water (e_d). K , eddy diffusion coefficient (m² yr⁻¹); F_{as} , exchange flux atmosphere-ocean (mol m⁻² yr⁻¹).

residence times (with respect to air-sea exchange) are 7.9 and 10.6 years. This can be compared to about 20 mol m⁻²yr⁻¹ obtained from an inventory of bomb ¹⁴C (see next paragraph). The value of 13.3 mol m⁻²yr⁻¹ therefore appears rather low.

The CO₂ flux per square meter from air to sea is given by swC_a , where s = CO₂ solubility, w = transfer velocity (piston velocity) for gas exchange, C_a = atmospheric CO₂ concentration. The solubility s varies with temperature, being higher for cold water than for warm water; transfer velocities for gas exchange, determined from radon measurements, were found to be higher in the Antarctic Ocean than elsewhere [Peng *et al.*, 1979]. From the data of Peng *et al.* (transfer velocities for actual water temperatures, not normalized to 20°C) and solubilities, I estimate that the flux in the outcrop area may be 1.7 times as large as for the rest of the ocean surface. Therefore, $F_{ad} = 1.7 F_{am}$, and from (3) and the relation $F_{as} = (1 - a_c)F_{am} + a_c F_{ad}$, we find

$$k_{am} = \frac{(1 - a_c)F_{as}}{(1 + 0.7 a_c)h_a C_o} \quad (19)$$

$$k_{ad} = \frac{1.7 a_c F_{as}}{(1 + 0.7 a_c)h_a C_o}$$

The vertical ¹⁴C profile in the deep sea depends on the eddy diffusivity K and the CO₂ exchange flux through the outcrop. It is found to be

$$R_{do}(z) = \frac{R_{ao}}{1 + \lambda/k_{da}^*} + \left(R_{mo} - \frac{R_{ao}}{1 + \lambda/k_{da}^*} \right) \cdot \frac{\cosh([h_d - z]/h_R)}{\cosh(h_d/h_R)} \quad (20)$$

where

$$h_R = \sqrt{K/(\lambda + k_{da}^*)}$$

The eddy diffusivity K is determined such that (20) reproduces the ¹⁴C values $R_{mo} = 0.95$ and $R_{ao} = 0.84$. For $a_c > 0$, K becomes smaller than for $a_c = 0$ (BD model) because of the direct ventilation through the outcrop; the rate of vertical (cross-isopycnal) transport into the deep sea decreases with increasing outcrop area in favor of increasing direct atmosphere-deep sea exchange. Values for K are given in Table 2. The eddy diffusivity found for the BD model is 4005 m²yr⁻¹ or 1.27 cm²s⁻¹. The values obtained for the OD model are lower, e.g., 2224 m²yr⁻¹ or 0.70 cm²s⁻¹ for $a_c =$

0.1, but still higher than those determined for actual vertical (cross-isopycnal) mixing in limited areas, typically 0.1 cm²s⁻¹ and less [Rooth and Östlund, 1972; Gargett, 1976; Jenkins, 1980]. It should be emphasized, however, that eddy diffusion in a global model is a concept summarizing quite different physical mixing and transport processes (partly or fully including deepwater formation) and can therefore not be directly compared with turbulent diffusion on a local scale. Steady state ¹⁴C profiles for the BD model ($a_c = 0$) and the OD model ($a_c = 0.1$) are shown in Figure 2. The vertical ¹⁴C distribution is very similar in both cases; obviously, it is but little affected by the outcrop feature.

BOMB-PRODUCED ¹⁴C

An important model test is the distribution of bomb ¹⁴C. If a model correctly simulates atmosphere-ocean exchange and ocean mixing, it should be able to reproduce the mean sea surface concentrations and the total oceanic inventory of bomb-produced ¹⁴C [see Broecker *et al.*, 1980].

Instead of using as model input the amounts of artificially injected ¹⁴C, which are not very precisely known, the mean

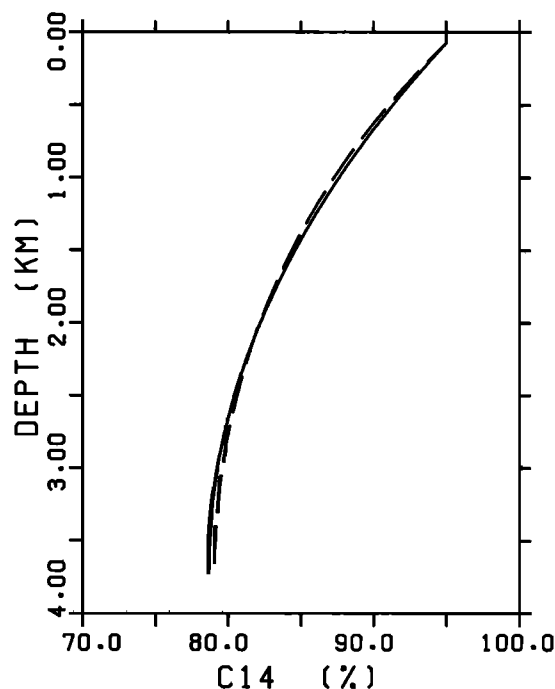


Fig. 2. Stationary ¹⁴C profile for the box-diffusion ocean model ($a_c = 0$; solid line) and for the outcrop-diffusion ocean model ($a_c = 0.1$; dashed line).

TABLE 3. Numerical model results for box-diffusion model ($a_c = 0$) and outcrop-diffusion model ($a_c = 0.1$)

Year	N_a	ν_a	ν_m	R_a	R_m	R_d
<i>Calibration with Preindustrial ¹⁴C ($a_c = 0.0$, $K = 4005$ m²/yr, $F_{as} = 18.0$ mol/M²/yr)</i>						
1860	292.80	0.0	0.0	100.00	95.00	84.00
1950	310.40	0.0601	0.566E-2	97.97	94.14	83.92
1960	316.35	0.0804	0.743E-2	122.50	96.63	83.96
1970	325.99	0.1133	1.024E-2	155.00	111.06	84.67
1980	340.76	0.1638	1.451E-2	131.00	111.58	85.22
<i>($a_c = 0.1$, $K = 2224$ m²/yr, $F_{as} = 13.3$ mol/m²/yr)</i>						
1860	295.80	0.0	0.0	100.00	95.00	84.00
1950	311.13	0.0518	0.479E-2	97.79	94.17	83.92
1960	316.29	0.0693	0.626E-2	122.50	96.12	83.95
1970	324.85	0.0982	0.867E-2	155.00	108.31	84.53
1980	337.98	0.1426	1.237E-2	131.00	109.53	85.01
<i>Calibration with Bomb ¹⁴C ($a_c = 0.0$, $K = 7685$ m²/yr, $F_{as} = 20.6$ mol/m²/yr)</i>						
1860	295.00	0.0	0.0	100.00	95.37	89.21
1950	310.87	0.0538	0.498E-2	98.20	94.68	89.11
1960	316.25	0.0720	0.654E-2	122.50	97.00	89.17
1970	325.06	0.1019	0.905E-2	155.00	110.06	90.07
1980	338.55	0.1476	1.288E-2	131.00	110.39	90.76
<i>($a_c = 0.1$, $K = 5180$ m²/yr, $F_{as} = 19.3$ mol/m²/yr)</i>						
1860	298.54	0.0	0.0	100.00	95.94	90.06
1950	311.66	0.0439	0.409E-2	98.23	95.26	89.99
1960	316.16	0.0590	0.537E-2	122.50	97.42	90.02
1970	323.70	0.0843	0.750E-2	155.00	110.01	90.93
1980	335.20	0.1228	1.077E-2	131.00	110.65	91.64

N_a —atmospheric CO₂ (ppm); ν_a , ν_m —relative CO₂ excesses in atmosphere and mixed layer; R_a , R_m , R_d —¹⁴C concentration in atmosphere, mixed layer, and deep sea.

observed atmospheric concentrations as compiled by Tans [1981] were prescribed from 1955 onward. After 1974 the values had to be estimated. The model results for the mixed layer ¹⁴C concentrations are given in Table 3 and Figure 3; in Figure 3 the mean observed values [Tans, 1981] are also shown. The BD model curve (solid) fits the data well, in general, except in the early 1960's (at that time there were large concentration differences, e.g., with latitude, and the corresponding mean values are not very precisely known), and after 1970 when the model results are somewhat high. The OD ($a_c = 0.1$) model (short-dashed curve in Figure 3) yields too low mixed-layer concentrations throughout.

The average oceanic inventory of excess ¹⁴C over the prebomb levels, as of 1973 (time of the GEOSECS program), has been estimated by Broecker *et al.* [1980] to 1.44×10^{-10} mol m⁻² for the world ocean and by Stuiver *et al.* [1981] to 1.37×10^{-10} mol m⁻² for the Pacific plus Atlantic oceans between 50°N and 50°S. The model inventory was calculated as

$$\int_0^{h_{oc}} C[R(1973) - R(1950)] dz \quad (21)$$

For the total CO₂ concentration C , its surface value (2.052 mol m⁻³) was assumed. In this way the increase of total CO₂ from 1950 to 1973 is neglected, but this is consistent with the method of Stuiver *et al.* The BD result is 1.20×10^{-10} mol m², the OD ($a_c = 0.1$) result is 0.99×10^{-10} mol m⁻². Thus both model versions yield too low inventories when compared to observation. The discrepancy appears significant, although the experimental estimates are probably not more accurate than 10–15% because they depend on the assumed prebomb ¹⁴C levels, which are not very well known.

Since the models do not correctly reproduce the bomb ¹⁴C uptake (time scale ~10 years), it must be suspected that they

also cannot well simulate the uptake of fossil CO₂, which has a similar time scale (22 years). Therefore, instead of using preindustrial ¹⁴C (time scale ~1000 years) for calibrating the model, it appears more adequate to use bomb-produced ¹⁴C [Broecker *et al.*, 1980]. The criteria chosen here for calibration with bomb-produced ¹⁴C are that the model must reproduce a ¹⁴C concentration of 111.0% in the mixed layer and an oceanic inventory of 1.40×10^{-10} mol m⁻² at the beginning of 1973. By an iterative method, the eddy diffusivity K and the average exchange flux F_{as} were adjusted so that these criteria were met; this was done for outcrop areas $a_c = 0$ (BD) and $a_c = 0.1$. Simultaneously, the preindustrial CO₂ level N_{ao} was adjusted such that the model yielded 315.6 ppm for 1959.

The resulting values for K and F_{as} (Table 2) are higher than obtained by the calibration based on preindustrial ¹⁴C. The exchange flux of about 20 mol m⁻² yr⁻¹ is compatible with

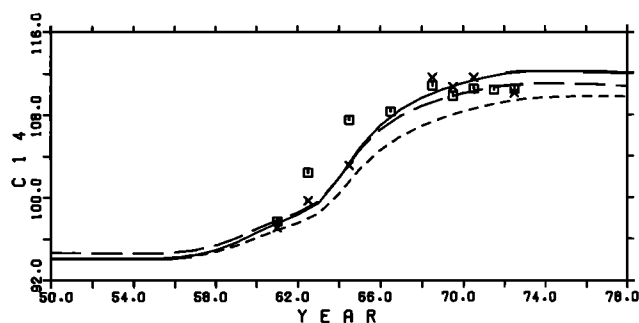


Fig. 3. Bomb ¹⁴C levels in the warm mixed layer according to different model versions. Solid curve, $a_c = 0$ (calibration: natural ¹⁴C); short-dashed, $a_c = 0.1$ (calibration: natural ¹⁴C); long-dashed, $a_c = 0.1$ (calibration: bomb ¹⁴C). Observed mean values [Tans, 1981]: x, southern hemisphere, □ northern hemisphere. Horizontal axis: year, vertical axis: ¹⁴C, percent.

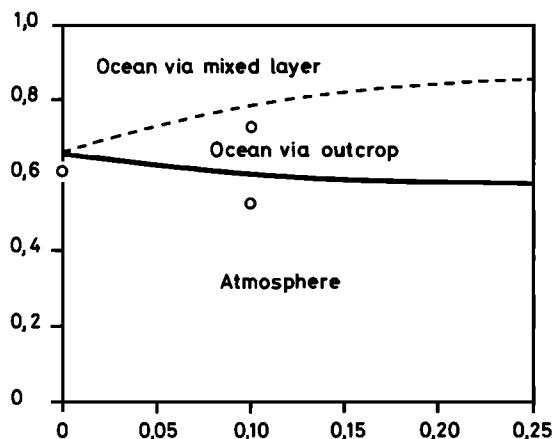


Fig. 4. Partitioning of excess CO₂ between atmosphere and ocean for an exponential CO₂ increase (e folding time $\mu^{-1} = 22.5$ yr) as a function of relative outcrop area a_c for calibration by natural ¹⁴C. Oceanborne fraction is subdivided into uptake through outcrop area and via mixed layer. Circles: partitioning for calibration with bomb-produced ¹⁴C (only $a_c = 0$ and $a_c = 0.1$).

the former BD value of 18.0 mol m⁻² yr⁻¹, and the resulting preindustrial ¹⁴C concentrations in the mixed layer, 95.4 and 95.9% for outcrop areas of 0 and 0.1 (see Table 3), are both within the limits of uncertainty of the existing data. However, the mean ¹⁴C values for the deep sea (89.2 and 90.1%) are clearly too high. Obviously, it is not possible to simultaneously simulate, in a satisfactory way, both preindustrial and bomb ¹⁴C inventories in the ocean with the simple models presented here.

For the outcrop areas the model yields a very small increase caused by bomb ¹⁴C—only about 1% (Table 3). At several GEOSECS stations in the Antarctic Ocean (five stations in the Atlantic south of 56°S, one station in the Pacific at 69°S, four stations in the Indian Ocean south of 53°S), very low surface concentrations between 92 and 99% were still observed from 1972 to 1974 [Östlund and Stuiver, 1980; Stuiver and Östlund, 1980; Östlund *et al.*, 1980]. For surface waters of the Weddell Sea, known as the principal source of Antarctic bottom water, Weiss *et al.* [1979] measured values between 88 and 92%. These authors estimated ¹⁴C values of 85.2% (preindustrial) and 88.1% (1973) for newly formed Weddell Sea bottom water; the difference of 3% is indeed comparable to the result of the OD model for the mean deep-sea increase. In two surface water samples from the Ross Sea, taken in 1976 under seasonal sea ice near McMurdo (77°52'S, 166°26'E), Loosli [1983] measured an ³⁹Ar concentration of about 77% modern and a ⁸⁵Kr concentration of 12 dpm per cc STP Kr (atmospheric concentration at that time: 24 dpm/cc). The ¹⁴C concentration was 91%. For a 100-m-thick water layer, the characteristic time for ³⁹Ar and ⁸⁵Kr equilibration is only about 30 days, assuming a global average value for the gas exchange rate. Thus the ³⁹Ar and ⁸⁵Kr clearly indicate a rather short residence time (~1 month) of the water at the surface.

The extent of these regions of very active exchange between surface and deep layers is difficult to estimate. Including the region of deepwater formation in the North Atlantic, they probably cover several percent of the global ocean, and a value of 10% may even be realistic. In addition to these areas, the outcrop feature of the model also represents regions of direct ventilation of thermocline waters.

Thus the effective value of the relative outcrop area a_c may be in the range of 0.05 to 0.15.

CO₂ RESPONSE TO FOSSIL INPUT

The fossil CO₂ production rate has steadily grown, and since World War II the growth was approximately exponential, with an e folding time of 22.5 yr. The model equations with constant ξ_m and ξ_d can be solved analytically for an exponentially increasing CO₂ input rate $q(t) = q_0 e^{\mu t}$. The concentrations in the different reservoirs then also increase exponentially, with the consequence that the ratio of the amount of fossil CO₂ in the different reservoirs remains constant. The vertical (relative) concentration profile of excess CO₂ in the ocean is

$$\nu_d = \frac{\nu_a}{\xi_c + \mu/k_{da}} + \left(\nu_m - \frac{\nu_a}{\xi_c + \mu/k_{da}} \right) \exp(-z/h_{ex}) \quad (22)$$

h_{ex} is the characteristic depth of the exponentially decreasing part of the excess CO₂ profile:

$$h_{ex} = \sqrt{\frac{K}{\mu + \xi_d k_{da}}} \quad (23)$$

The mixed layer excess is found to be

$$\nu_m = \frac{\nu_a(k_{ma}h_m A_m + k_{da}h_{ex} A_{oc})}{(\mu + \xi_m k_{ma})h_m A_m + K A_{oc}/h_{ex}} \quad (24)$$

The fraction of the cumulative fossil production residing in the atmosphere (airborne fraction) is obtained as

$$r_a = \frac{h_a}{h_a + h_1 + h_2}$$

where

$$h_1 = \frac{k_{da}(h_d - h_{ex})}{(\mu + \xi_d k_{da})} \quad (25)$$

$$h_2 = \frac{(h_m[1 - a_c] + h_{ex})(k_{ma}h_m[1 - a_c] + k_{da}h_{ex})}{(\mu + \xi_m k_{ma})h_m(1 - a_c) + K/h_{ex}}$$

As mentioned above, the data indicate an airborne fraction $r_a = 0.55$ for the period 1959–78. The pure BD case (outcrop area $a_c = 0$; first method of calibration) yields $r_a = 0.667$ (Table 2), i.e., the ocean takes up considerably less than the observed nonairborne fraction, the 'ocean-borne' fraction of the cumulative input r_{oc} being 0.333. For $a_c = 0.10$, $r_a = 0.605$ ($r_{oc} = 0.395$), i.e., the oceanic uptake capacity is about 20% larger than for the BD model, both model versions being calibrated with the same preindustrial ¹⁴C values.

In order to obtain the same airborne fraction (0.605) with the BD model, an eddy diffusivity of 9000 m²yr⁻¹ (2.7 cm²s⁻¹) would have to be assumed (keeping the BD value for F_{as} , 17.99 mol m⁻²yr⁻¹). With the numerical model version using the actual production history, the airborne fraction for the period 1959–1978 is unchanged for $a_c = 0$ (0.666) compared to the analytical solution, but slightly lower for $a_c = 0.1$ (0.592). If the outcrop area is increased beyond $a_c = 0.10$, the oceanic uptake does not grow much further and the airborne fraction does not become much lower (cf. Figure 4 and Table 2). On the other hand, even a rather small outcrop area already leads to a noticeably enhanced net flux into the

ocean: for $a_c = 0.02$, the fraction of fossil CO₂ taken up by the ocean r_{oc} is 0.353, 6% more than for the BD model without outcrop ($r_{oc} = 0.333$).

If the models are calibrated by means of bomb ¹⁴C, the oceanic uptake is larger than if they are calibrated with preindustrial ¹⁴C. For the BD model the analytically calculated airborne fraction (Table 2) is 0.611 (numerical computation: 0.608); for the OD model with $a_c = 0.1$, it is 0.528 (numerical computation: 0.521). These values are about 10% lower than those obtained with the first calibration method. This is so because both transport parameters, air-sea exchange flux, and eddy diffusivity are higher if determined from bomb ¹⁴C than from preindustrial ¹⁴C. The model results for outcrop areas 0 and 0.1 now embrace the observed airborne fraction of 0.55. Taking into account the uncertainties of this observed value, a modest additional net input from biomass destruction is compatible with the OD model, but our results seem to indicate that an airborne fraction of less than 50%, as required by some high estimates of the biosphere input, is not compatible with what is known about air-sea exchange and oceanic circulation.

It is interesting to consider how much of the total excess CO₂ has entered the ocean via the mixed layer and how much via the deep-sea outcrop. These values, indicated by the symbols r_m and r_d , are represented in Table 2 and Figure 4. For $a_c = 0.10$, nearly half of the 'ocean-borne' excess CO₂ has entered through the outcrop for both calibration methods, which shows that this area is a rather effective CO₂ sink. This can be analyzed further by considering what degree of equilibration with atmospheric excess CO₂ the surface water has reached. The degree of equilibration in the mixed layer is

$$e_m = \frac{\text{excess } p\text{CO}_2 \text{ in mixed layer}}{\text{excess } p\text{CO}_2 \text{ in atmosphere}} = \frac{\xi_m c_m}{c_a} \quad (26)$$

(c_a , c_m = concentrations of excess carbon). The net CO₂ flux density from atmosphere to mixed layer is given by

$$F_{\text{am,net}} = s w (c_a - \xi_m c_m) = s w c_a (1 - e_m) \quad (27)$$

i.e., it is proportional to $(1 - e_m)$. In the outcrop areas the water is much farther from equilibrium ($e_d \sim 0.1$ to 0.2 ; cf. Table 2) than in the mixed layer ($e_m \sim 0.8$), and the net CO₂ flux per square meter is considerably larger. The reason for the different degrees of equilibrium is that oceanic uptake of excess CO₂ via the mixed layer is essentially limited by downward eddy diffusion, while the transport resistance associated with air-sea gas exchange is less important. The rate of uptake via outcrop is, however, limited only by the finite rate of gas exchange, since mixing along the isopycnals is infinitely fast, so that the CO₂ is immediately diluted into the whole deep-sea reservoir.

ATMOSPHERIC ¹⁴C DILUTION (SUESS EFFECT)

The atmospheric ¹⁴C/C ratio has been perturbed by man-made processes in two ways: dilution by (¹⁴C-free) fossil CO₂ (Suess effect) and injection of bomb-produced ¹⁴C. In the linearized approximation (cf. (15)) the Suess effect corresponds to a 'negative input' of ¹⁴C. Until 1950, the cumulative fossil CO₂ production amounted to 10% of the preindustrial atmospheric CO₂; thus, if all CO₂ had remained in the atmosphere, the ¹⁴C concentration would have decreased from 100 to 91%. As a result of exchange with the ocean and

the biosphere, the Suess effect is, however, considerably less. Recent high-precision measurements yielded a decrease of 2.0% from 1860 to 1950 [Stuiver and Quay, 1981]. The same authors estimate that 0.3% of this decrease are due to natural processes (solar and geomagnetic variations) and that consequently the effect resulting from fossil CO₂ alone amounts to 1.7%. Results from numerical simulations are given in Table 3. For 1950 the calculated Suess effect (atmospheric ¹⁴C decrease) is slightly more than 2% for the calibration with preindustrial ¹⁴C, somewhat higher than the observed value but still in reasonable agreement with it. The results for both the BD and OD models, calibrated with bomb ¹⁴C, is 1.8%—in excellent agreement with observation. Thus this second method of calibration seems more appropriate also for simulating the ¹⁴C dilution.

The model-calculated Suess effect, in contrast to the CO₂ increase, is not smaller with an outcrop than without. Obviously, there is a marked contrast between oceanic uptake of excess CO₂ and of ¹⁴C perturbation. For the Suess effect the surface water is farther from equilibrium than for excess CO₂, and correspondingly, the oceanic dilution factor is larger for ¹⁴C than for CO₂. This is, of course, a consequence of the buffer factor, which affects CO₂ but not ¹⁴C, so that the diluting capacity of the ocean or of an oceanic subvolume is, at equilibrium, about 10 times smaller for CO₂ than for ¹⁴C.

For discussing ¹⁴C perturbations quantitatively, the dilution by the biosphere should be studied in more detail. For the Suess effect the biosphere, as modeled here, yields the same effective diluting carbon mass as the atmosphere. This is not discussed further here because the emphasis of this study is on the role of the ocean.

MODEL RESPONSES FOR NONEXPONENTIAL CO₂ INPUTS

As long as a model is linear—in our case as long as the buffer factors can be assumed constant—its behavior can be fully characterized by the response to a pulse input of excess CO₂ into the atmosphere. If $R(t - t_0)$ is the response to a pulse at time t_0 , then the atmospheric concentration excess for an arbitrary production rate function $q(t)$ is given by

$$c_a(t) = \int_{-\infty}^t q(t_0) R(t - t_0) dt_0 \quad (28)$$

In Figure 5 the pulse responses are represented for the model version calibrated with preindustrial ¹⁴C (solid lines, curve 1; BD, curve 2; OD model, $a_c = 0.1$) as well as for those calibrated with bomb ¹⁴C (dashed lines, curve 3; BD, curve 4; OD model). For these calculations, constant buffer factors were assumed. For each calibration method the CO₂ level becomes considerably lower for OD than for BD, obviously because the deep-sea outcrop forms a rather efficient sink. On the other hand, for each outcrop area (0 or 0.1) the bomb-¹⁴C-calibrated transport parameters lead to a more rapidly decreasing CO₂ level than those determined from preindustrial ¹⁴C.

The different characteristics of the two models have important consequences for longer-term predictions of atmospheric CO₂ levels. To demonstrate this, simulation results are shown in Figure 6 for an upper-limit scenario where all economically exploitable fossil fuels, equivalent to $8 N_{ao}$, are burnt before the year 2200. The results are presented as model sensitivity tests and are not supposed to be actual

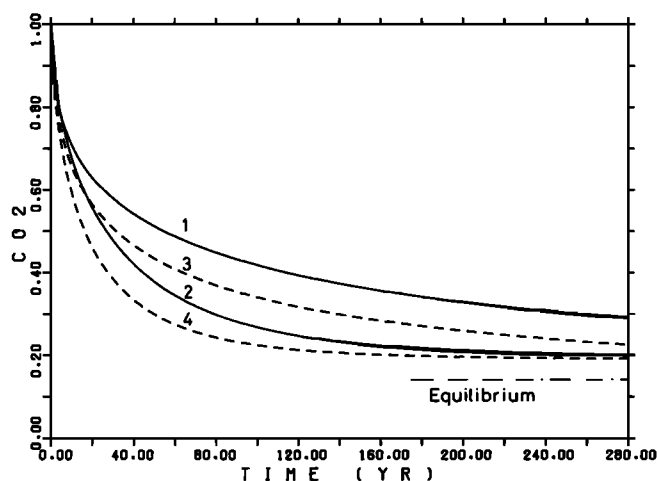


Fig. 5. Atmospheric CO₂ levels (relative units) after a pulse input into the atmosphere for model versions without outcrop (BD model, curves 1 and 3) and with relative outcrop area $a_c = 0.1$ (curves 2 and 4). Calibration by natural ¹⁴C, solid curves; by bomb-produced ¹⁴C, dashed curves.

predictions. The assumed production rate (short-dashed line in Figure 6) is given by

$$q(t) = \frac{d}{dt} \frac{P_\infty}{1 + (P_\infty/P_1 - 1) \exp[-\mu(t - t_1)]} \quad (29)$$

P_1 and P_∞ are the cumulative production rates at times t_1 (1980) and $t = \infty$; $\mu = 1/22.5$ yr. The maximum input rate, about 10 times as large as the 1980 production, occurs around 2060, the maximum level 45 to 80 years later. The maximum concentrations observed are between 1210 and 1990 ppm, depending on the model version and the calibration; this can be compared to a final level of 2630 ppm, reached if all the CO₂ would remain in the atmosphere. The relatively high airborne fractions are partly caused by the large buffer factors connected with high CO₂ levels (equation (16)). The great difference between the results obtained with (curves 2, 4) and without (curves 1, 3) outcrop clearly demonstrates that direct ventilation of deep-sea and thermocline waters is an important path for CO₂ uptake by the ocean. For this scenario the method of calibration is of secondary importance, as shown by Figure 6.

When considering the results shown in Figures 5 and 6, it should be kept in mind that the model ocean is a grossly oversimplified representation of nature, mainly regarding the infinitely fast, quasihorizontal mixing by which fossil CO₂ entering through the outcrop is immediately mixed into the whole deep sea. Thus, the BD model without outcrop and the OD model with $a_c = 0.1$ can be regarded as extreme cases with respect to the role of the direct exchange atmosphere-deep sea, the real ocean being situated somewhere in between.

CONCLUSIONS

By inclusion of a deep-sea outcrop through which the atmosphere is in direct contact with the large volumes of the deep ocean, the calculated oceanic uptake of excess CO₂ is increased if the different model versions are calibrated consistently in the same way. The oceanic dilution factor, defined as the amount of excess CO₂ in the ocean relative to that in the atmosphere [Oeschger *et al.*, 1980], has a value of 0.50 for the pure BD model calibrated by natural ¹⁴C, 0.65 if

an outcrop area covering 10% of the ocean is present, and 0.89 if the model with this outcrop area is calibrated by means of bomb-produced ¹⁴C. The corresponding airborne fractions of fossil CO₂ are 67%, 60% and 53% (observed: 55%). The influence of the outcrop is significant, and this feature should be taken into account in future modeling work. The OD model may be called 1 1/2-dimensional, in contrast to purely one-dimensional BD or two-box ocean models. By showing the role of deepwater outcrop, it may be of help when establishing two- or three-dimensional models.

The method of calibration is obviously important also. The preindustrial distribution of ¹⁴C is adequate for simulating phenomena with long characteristic times, such as the distribution of properties in intermediate and deep waters. For phenomena with time scales of one to a few decades, however, such as the CO₂ increase caused by fossil fuel combustion, a calibration based on nuclear-weapon-produced ¹⁴C is more appropriate.

The results presented here suggest that the airborne fraction for the time period 1959 to 1978 probably was in the range of 53–61%, taking as limits the results of the bomb-¹⁴C-calibrated model versions, with relative outcrop areas between 0 and 0.1 if fossil fuel is considered alone. This means that any net additional input must have been small, at most about 10% of the fossil input, assuming that the corresponding input rate increased similarly as the fossil CO₂ production rate. Since the carbon release by biomass destruction is generally estimated to have been larger,

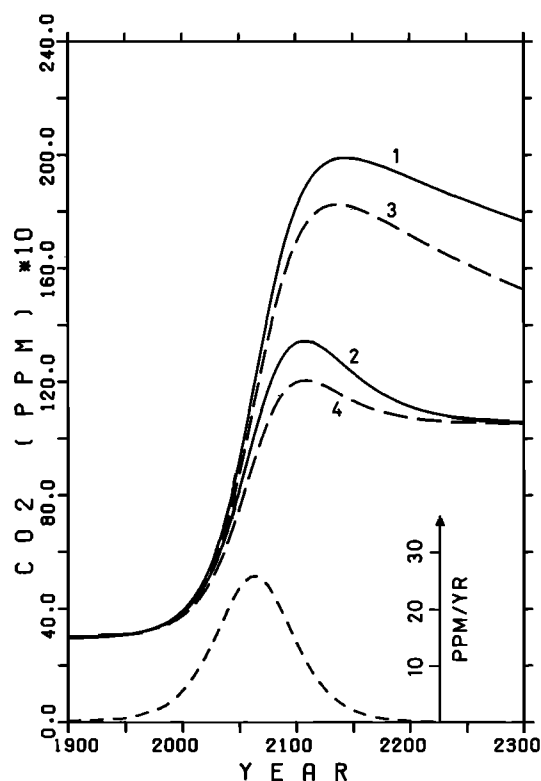


Fig. 6. Model-calculated CO₂ levels for an upper-limit production scenario where all exploitable fossil fuels are burnt, for model versions without outcrop (BD model, curves 1 and 3) and with relative outcrop area $a_c = 0.1$ (curves 2 and 4). Calibration by natural ¹⁴C, solid curves; by bomb-produced ¹⁴C, dashed curves. Notice that vertical scale goes from 0 to 2400 ppm. Short-dashed curve: production rate. The results must be regarded as model sensitivity test, not as actual prediction.

typically 20–50% of the fossil amounts, it appears that the biosphere must have grown in nonexploited regions, which may have been the effect of fertilization by excess CO₂ and by anthropogenically released phosphorus and nitrogen. The picture may change somewhat if there occurred a major CO₂ input in the past, e.g., by a pioneer agricultural activity. If such a large input occurred only a few decades ago, it would still influence the present CO₂ levels by providing a decreasing atmospheric baseline because the ocean would still take up some of the corresponding excess CO₂ [Siegenthaler *et al.*, 1978].

The fact that the simple diffusive ocean models considered here are not capable of simultaneously reproducing both the observed distributions of natural and bomb-produced ¹⁴C demonstrates that they have to be modified for correctly simulating processes with short and long time scales. It will be necessary to take into account that isopycnals intersect the surface at all latitudes and that the ratio of outcrop area to volume—showing the importance of direct ventilation, represented by the parameter k_{da} in this paper—is larger for shallow than for deep-ocean layers. Furthermore, the finite rate of quasihorizontal mixing along the isopycnals must be taken into consideration. Once a satisfactory model for the water exchange in the ocean is available, nutrient cycles can be studied by including the transport by biogenic particles.

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